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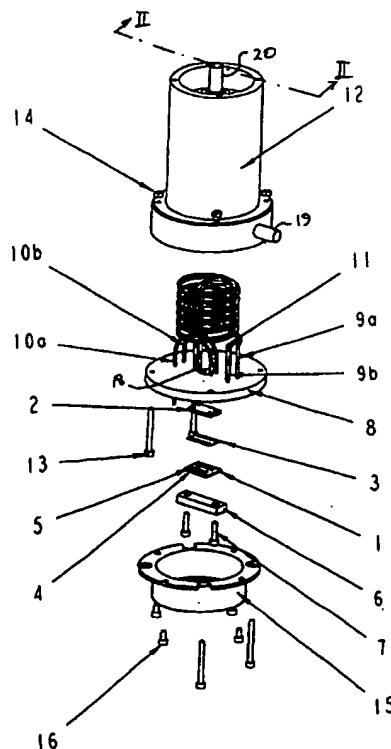
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(71) Applicant (for all designated States except US): CAMBRIDGE CONSULTANTS LIMITED (GB/GB); Science Park, Milton Road, Cambridge CB4 4DW (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): EDGSON, Raymond, Anthony (GB/GB); 148 The Rowans, Milton, Cambridge CB4 6YX (GB). WILKINSON, Eric (GB/GB); 14 Chequers Croft, Hilton, Huntingdon, Cambridgeshire PE18 9PD (GB).			
(74) Agent: COZENS, Paul, Dennis; Mathys & Squire, 100 Grays Inn Road, London WC1X 8AL (GB).			

(54) Title: METHOD AND APPARATUS FOR MEASURING AN ELECTRICAL PARAMETER OF A FLUID

(57) Abstract

A parameter (for example electrical conductivity) of a test fluid is measured in a measurement cell (1, 2, 3, 4) having two sets of electrodes in respective flow paths, which carry a test fluid and a reference fluid, respectively. The measurements are taken at the same time, and the temperature of the fluids is equalised by passing them through coiled tubing (10a, 10b) in a heat exchanger, and passing heat exchange fluid over a wall (2) of the cell in a plane midway between the two flow paths.



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Method and Apparatus for Measuring an Electrical
Parameter of a Fluid

5

This invention relates to a method of measuring an electrical parameter of a fluid. In particular it concerns the measurement of the electrical conductivity of liquids.

- 10 Electrical conductivity is a property of a liquid, which may be used in the identification of liquids and the measurement of the concentration of certain constituents of a solution or mixture of different materials, including bubbles and solids in a liquid medium. The principle of such concentration measurement is that the constituents have a different electrical conductivity to that of the base
- 15 material, such that the electrical conductivity of the combination varies with the concentration.

The electrical conductivity is measured by passing an electrical current through the liquid and calculating the electrical resistance from the voltage drop across

20 the liquid divided by the current. This is done in a device called a conductivity cell, which contains at least two electrodes separated by the liquid to be measured. The electrical current enters and leaves the liquid via electrodes, which are normally arranged so that they are electrically insulated from one another apart from the liquid path.

25

The electrical conductance is calculated as the inverse of the electrical

resistance. This electrical conductance depends not only on the electrical conductivity, but also on the geometry of the electrical path through the liquid and any additional electrical paths (which are normally minimised). In many situations, the conductance C is related to the conductivity ρ by a simple
5 constant k (which is usually termed the cell constant) as shown in equation 1.

$$\rho = k C \dots\dots\dots 1$$

This relationship follows from simple electrical theory, which states that the
10 conductance equals the conductivity times the conductor cross sectional area divided by the conductor length. In other words, the cell constant equals the conductor length divided by the conductor cross sectional area. Conventionally, the cell constant is established by calibrating the conductivity cell with a liquid of known conductivity – typically potassium chloride.

15 To prevent polarisation of the electrodes, whereby an excess (or deficit) of charge builds up at and around the point at which the electrical signal enters and leaves the fluid, alternating current is conventionally used instead of direct current.

20 Conductivity cells may be arranged to accept a flowing liquid or to measure a static pool of liquid according to the nature of the application.

The conductivity of a liquid depends on temperature – a change of about 2%

per degree centigrade is fairly typical. In many conductivity measuring devices, therefore, a temperature probe is used to measure the temperature, so that a correction may be made for any difference between the actual measurement temperature and the reference temperature (which is often 25°C).

5

Accurate temperature compensation is however difficult for a number of reasons. The first of these is that the point and time at which the temperature is measured is not (in general) the same point and time at which the conductivity is measured. Thus any change in the temperature between the
10 temperature measurement and the conductivity measurement results in an error. This problem is exacerbated by the fact that both the temperature measurement and the conductivity measurement usually generate heat as a by product of the measurement technique. At low flow rates, these heating effects have a greater affect on the temperature of the fluid and, at the same time, the
15 temperature probe must be better isolated from the environment to ensure that heat is neither added nor removed from the liquid by the temperature probe. The lower the flow rate, however, the greater the errors introduced by these problems such that the accuracy which can be obtained with known techniques reduces as the flow rate reduces.

20

These problems also affect the calibration of the cell when the temperature must also be known very accurately. This means that the errors are encountered twice in the total measurement process, rather than just at the time of the conductivity measurement of the test liquid. In addition, if the

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variation of the conductivity with temperature is not accurately known for both the calibration liquid and the test liquid, further errors may be generated in the temperature correction process.

- 5 An additional problem with conductivity cells is that the cell constant may change with time and regular re-calibration is required if accurate performance is to be maintained.

WO-A-9 604 401 discloses methods and apparatus for measuring the
10 differential conductivity of decomposed and undecomposed area solutions. The present invention is also applicable to such application, and the entire disclosure of WO-A-9 604 401 is incorporated herein by reference.

According to one aspect of the present invention there is provided a method of
15 measuring an electrical property of a test fluid comprising the steps of:

- a) providing measurement cell means containing separate bodies of said test fluid and a reference fluid respectively, said bodies being at substantially the same temperature, and
20
b) measuring the electrical parameter of said body of test fluid and said body of reference fluid at substantially the same time.

Preferably the test fluid and reference fluid are in thermal proximity with one

another.

Preferably the temperatures of the test fluid and reference fluid are equalised prior to the measurement.

5

Thereby, the temperature related errors in the measurement can be reduced.

In one embodiment the reference fluid has a known value of the parameter and is used as a calibration fluid to calibrate the measurement of the electrical
10 property of the test fluid.

In another embodiment a differential measurement is made and it is not necessary for the parameter of the reference fluid to be known.

15 Preferably, the method further comprises placing the test fluid and the reference fluid in separate cells which are in thermal contact and more preferably comprises a further step of passing the test fluid and reference fluid through a pair of secondary coils in a heat exchanger to ensure thermal equilibrium of the fluids. The reference fluid preferably undergoes a
20 modification step which alters the electrical property of the reference fluid and advantageously the reference fluid is the same as the test fluid.

In another aspect, the invention provides apparatus for determining an electrical parameter of a test fluid in relation to that of a reference fluid, comprising test

cell means arranged to receive a body of said test fluid and a body of said reference fluid and heat exchange means for generating a flow of primary heat exchange fluid in thermal proximity to said bodies of test fluid and reference fluid.

5

Rather than attempting to measure the temperatures of the calibration fluid and the test fluid accurately, the electrical conductivities of the two fluids are preferably measured at essentially the same time as each other using a pair of cells which are in close thermal proximity to one another, such that a
10 substantial temperature difference cannot exist between them. Most of the temperature related errors then cancel out and there is no heating generated by the temperature measurement.

Preferably said primary heat exchange fluid flows over one surface of a metal
15 wall, and a wall of said measurement cell means is disposed against an opposite surface of said metal wall.

Preferably said measurement cell means is thermally symmetrical about a plane midway between said bodies of test fluid and reference fluid, said bodies being
20 symmetrically disposed about said plane.

Preferably said heat exchange means comprises a metal wall having one surface in contact with said measurement cell means and an opposite surface in contact with said flow of primary heat exchange fluid.

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To make sure that the temperatures of the two liquids are the same as each other as they enter their respective cells, they may optionally be passed through a pair of secondary coils of a heat exchanger, which is preferably also used to control the temperature of the cells. The temperature of the liquid in the cells can be measured indirectly by measuring the temperature of the liquid in the primary flow path of the heat exchanger. The flow rate through the primary path can generally be higher because the primary liquid can be recirculated, whereas the test fluid is often only available in limited quantities. This means that the temperature can be measured more readily without the limitations described above.

As noted above, two preferred modes of operation are possible, namely one in which the reference liquid is a calibration liquid, whose electrical conductivity has been characterised under exacting conditions, with ample quantities and time for each measurement, and a second in which a differential measurement is made. This differential mode is particularly relevant when a liquid can be split into two paths, with the conductivity of one path being modified by some process before the conductivities of both paths are compared. In this case, the important factor is the change caused by processing one path (rather than the absolute value of the conductivity).

In the first case, the temperature need not be measured (directly or indirectly) as shown by the following analysis:

Let the electrical conductivity of cell a be given by the following equation:

$$\rho_a = \rho_{a25} + \alpha_a (T_a - 25) \dots\dots\dots 2$$

5 where ρ_a = measured electrical conductivity in cell a

T_a = temperature in cell

ρ_{a25} = electrical conductivity of fluid in cell a at 25 °C

α_a = rate of change of electrical conductivity with temperature

10 This is the equation used with single cell conventional measurements and it will be appreciated that an error in the temperature measurement leads directly to an error in the conductivity.

For twin cell measurement, a similar equation can be written for the second

15 cell:

$$\rho_b = \rho_{b25} + \alpha_b (T_b - 25) \dots\dots\dots 3$$

where ρ_b = measured electrical conductivity in cell a

20 T_b = temperature in cell

ρ_{b25} = electrical conductivity of fluid in cell a at 25 °C

α_b = rate of change of electrical conductivity with temperature

Provided the temperatures T_a and T_b are equal, these two equations can be

combined to give an expression for the conductivity of the fluid in cell b in terms of the two cell measurements and the known properties, but without knowledge of the temperature. Thus the conductivity of the fluid in cell b referred to 25 °C is:

5

$$\rho_{b25} = \rho_b + (\rho_{a25} - \rho_a) \alpha_b / \alpha_a \dots\dots\dots 4$$

For the second mode of operation, the differential referred to 25°C ($\rho_{b25} - \rho_{a25}$) can be found, again provided $T_a = T_b$:

10

$$\rho_{b25} - \rho_{a25} = \rho_b - \rho_a + 25 (\alpha_b - \alpha_a) - T (\alpha_b - \alpha_a) \dots\dots\dots 5$$

Although this is not completely independent of temperature, the accuracy with which the temperature must be known is less than for a single cell device, because α_b and α_a are normally equal or very close to each other. This means that the indirect temperature measurement technique described above is particularly suitable.

A similar analysis is applicable to the measurement of other electrical parameters, for example capacitance or dielectric loss tangent.

The use of two cells in the same device also allows for re-zeroing of the two cells against each other. This means that changes in the cell constant can be detected and a compensation made without the need for a re-calibration.

As previously mentioned, the two cells are preferably in close thermal proximity to each other and this is best achieved by making them from a material with a high thermal conductivity, but low electrical conductivity, to ensure that the electrodes are insulated from each other (except for the path through the liquid). Particularly suitable materials are alumina ceramic and sapphire or metals with an insulating coating such as glass. Close thermal proximity can also be enhanced by making the distance between the flows paths of the cells small and by making the entire construction symmetrical with respect to heat flows, so that there is no significant heat flow from one cell to the other (which would cause a temperature difference). Furthermore, the entire cell assembly should preferably be placed in close thermal proximity to the primary side of the heat exchanger by attaching the cells to a thermally conductive wall of the heat exchanger.

It will be understood that the measurement of the conductance of the electrical path through the liquid in the cell is achieved by conventional means and as such is not described in detail.

Other preferred features of this invention are defined in the dependent Claims.

20

A preferred embodiment of the present invention will now be described, purely by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is an exploded view of a cell and heat exchanger;

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Figure 2 is a cross-sectional view of a cell and heat exchanger taken on II-II of Figure 1;

Figure 3 is a cross-sectional view of one measurement cell taken parallel to II-
5 II; and

Figure 4 is a plan view of plate 8.

The embodiment shown in Figures 1 to 4 is considered first from the point of
10 view of the test liquids, which enter the secondary side of the heat exchanger via tubes 9a and 9b. These tubes are long enough to ensure that the two test liquids reach the same temperature as the primary heat exchanger liquid and each other within close limits. The tubes are made from a thermally conductive material such as steel, as this minimises the length of tube required for the
15 temperatures to stabilise. The tubes 9a and 9b are coiled together so that they are in close thermal proximity. This minimises the possibility of a temperature difference being established between them.

From the heat exchanger, these tubes pass directly into cell top plate 2, which
20 has holes to locate the tubes, which must be sealed with adhesive or other suitable means. After passing through these holes, the fluids enter flow channels in intermediate plate 3 such that they pass in flow paths 17 (Figures 3 and 4) over the electrodes on bottom plate 1. The liquids then flow back through the top plate and into exit tubes 10a and 10b, which may pass directly

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to the outside or else pass through the heat exchanger first if that is more convenient. The exit tubes 10a and 10b are also sealed with respect to the cell top plate 2. Further seals are employed where the tubes 9a, 9b, 10a and 10b pass through bulkhead plate 8, so as to prevent leakage of the primary heat
5 exchanger fluid.

A clamp plate 6 and screws 7 retain the bottom plate 1, the intermediate plate 3 and the top plate 2 to the bulkhead 8 with the aid of tapped holes in the bulkhead. Additionally, non-electrically conductive sealants such as epoxy
10 adhesives may be employed to ensure a seal between each of these components and also to ensure that no fluid passes from one flow path to the other. The sealant layer is best kept as thin as possible to ensure that all of these cell components remain as closely as possible the same temperature.

15 A cut-out 18 is provided in the bulkhead 8, as shown in Figures 2 and 4, so as to allow the primary heat exchanger fluid to be in direct thermal contact with the cell top plate 2. The bulkhead is preferably made from a thermally conductive material such as steel or another suitable metal, and is preferably as thin as possible to ensure a close thermal contact consistent with the need to maintain
20 a seal against the top plate 2. A temperature probe 11 such as a platinum resistance thermometer may be placed in the bulkhead 8 to measure the primary fluid temperature.

The heat exchanger primary fluid is within a cover 12, retained to the bulkhead

by screws 13 and nuts 14 and a seal such as a gasket (not shown). The cover 12 may be conveniently manufactured from a polymer material such as polypropylene. An inlet 19 and an outlet 20 are provided in the plane of Figure 2 within the cover 12 to allow the primary fluid to enter and leave the primary circuit, passing over the coils 9a and 9b in the process. These connections are preferably arranged so that the primary fluid enters and leaves in the plane of Figure 2, which lies centrally between the two flow channels in the intermediate plate 3 and perpendicular to the plane of the bulkhead 8. The whole arrangement is designed to minimise thermal asymmetries about this plane.

10

An additional cover 15, which is retained by screws 16, is designed to isolate the cell components 1, 2 and 3 from the environmental air, so as to maintain the cell and the primary fluid at a similar temperature and also to maintain the thermal symmetry about the plane described above. To ensure that the air around the cell components is kept close to the temperature of the heat exchanger, the primary liquid can be routed through the cover 15 or the space between the cover and the clamp plate 6 or even through the clamp plate 6. This is, however, a refinement which has not normally been found to be necessary.

20

The cell bottom plate provides a substrate for electrodes 4, which may be of vacuum deposited gold or platinum or other materials known in the art. Lead wires 5 carry the electrical signals to and from the electrodes. The electrode configuration may be any of those known in the art including the simplest two

electrode (per flow channel) arrangement which is not ideally suited to high accuracy measurement. A conventional four electrode measurement, with the outer electrode pair being used to deliver the power and the inner pair being used for sensing, is a particularly suitable configuration.

5

In the embodiment as shown in Figure 3, a seven electrode arrangement is shown, comprising a central electrode 4A of one polarity and two outer electrodes 4B of opposite polarity to electrode 4A. The resistance is determined by measuring the current between inner electrode 4A and outermost electrodes 10 4B, and by measuring the voltage i) between electrodes 4C and ii) between electrodes 4D in the standard manner.

The cell components 1, 2 and 3 are best manufactured from a material such as alumina or sapphire, which is electrically insulating but thermally conductive. 15 Other cheaper materials including polymers and glasses may be employed, but the performance is not quite as good.

The device described above was designed for the following operating conditions and has certain key dimensions as listed:

20

Conductivity range:	0 to 50 mS/cm (at 25°C)
Accuracy:	5 μ S/cm
Primary Flow Rate:	500 ml/min
Secondary flow rate:	1 ml/min (per channel)

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Max Difference Between

Inlet Temperatures: 10°C

Nominal Cell Constant: 50 cm⁻¹

Cell Channel Width: 1 mm

5 Cell Channel Height: 0.5 mm

Cell Gauge Length: 2.5 mm

Secondary Tube Length: 800 mm

Secondary Tube Bore: 1 mm

Secondary Tube Diameter: 1.6 mm

10

The invention is particularly suitable for use in analytical instruments for measuring the concentration of a particular substance in a liquid. Potentially any substance which can be converted (such as by a chemical reaction) into another substance which has a different electrical conductivity is suitable for
15 such a device. A further application is as a straight forward conductivity meter for liquids in laboratory or industrial processes. Another application is a reference meter for the calibration of other conventional cells.

It will be understood that the present invention has been described purely by
20 way of example, and that modifications of detail can be made within the scope of the invention. For example, two or more measurement cells in parallel could be thermally coupled to a common heat exchanger.

Claims

1. A method of measuring an electrical parameter of a test fluid comprising the steps of:

5
a) providing measurement cell means (1, 2, 3, 4) containing separate bodies of said test fluid and a reference fluid respectively, said bodies being at substantially the same temperature, and

10 b) measuring the electrical parameter of said body of test fluid and said body of reference fluid at substantially the same time.
2. A method according to Claim 1, wherein said bodies of fluid are in thermal proximity to each other.

15
3. A method according to Claim 1 or Claim 2 wherein the temperatures of said fluids are equalised prior to introducing them into said measurement cell means.
- 20 4. A method according to any preceding Claim, wherein said reference fluid is a calibration fluid whose said electrical parameter is known.
5. A method according to any of Claims 1 to 3 wherein said reference fluid is provided by subjecting test fluid to a process which changes said

electrical parameter and said measuring step b) involves a comparison of said electrical parameter of said body of test fluid with that of said body of reference fluid.

- 5 6. A method according to Claim 4 or Claim 5, wherein the measurement is standardised to a predetermined temperature on the basis of the relationship:

$$\rho_b(\theta) = \rho_b(\rho_a(\theta) - \rho_a).$$

10

where: $\rho_b(\theta)$ is the electrical parameter of the test fluid at a standard temperature θ ,

$\rho_a(\theta)$ is the electrical parameter of the reference fluid at standard
15 temperature θ ,

ρ_b is the electrical parameter of the test fluid at the measurement temperature,

20 ρ_a is the electrical parameter of the reference fluid at the measurement temperature,

α_b is the temperature coefficient of the electrical parameter of the test fluid, and

α_a is the temperature coefficient of the electrical parameter of the reference fluid.

7. A method according to Claim 4 or 5, wherein the temperature at which the measurement is made is determined, and the measurement is standardised to a predetermined temperature on the basis of the relationship:

$$\rho_b(\theta) - \rho_a(\theta) = \rho_b - \rho_a + 25(\alpha_b - \alpha_a) - T(\alpha_b - \alpha_a)$$

10

wherein T is said measurement temperature and the other symbols are as defined in Claim 6.

8. A method according to any preceding Claim wherein said electrical parameter is conductivity.

9. A method according to any preceding Claim wherein said measurement cell means (1, 2, 3, 4) is disposed in thermal proximity to flowing heat exchange primary fluid.

20

10. A method according to Claim 9, wherein heat exchange between said primary heat exchange fluid and said measurement cell means (1, 2, 3, 4) is thermally symmetrical about a plane midway between said bodies of test fluid and reference fluid, said bodies being symmetrically disposed

about said plane.

11. A method according to Claim 10, wherein said primary heat exchange fluid enters and leaves in said plane.

5

12. A method according to Claim 10 or Claim 11, wherein said primary heat exchange fluid flows over one surface of a metal wall, and a wall (2) of said measurement cell means (1, 2, 3, 4) is disposed against an opposite surface of said metal wall.

10

13. A method according to Claim 12, wherein said metal wall (2) has an aperture (18), which exposes the exterior of said wall (2) of said measurement cell means to flowing primary heat exchange fluid.

- 15 14. A method according to any of Claims 9 to 13, wherein a cover (15) covers a side of said measurement cell means disposed opposite a region of thermal proximity to said primary heat exchange fluid.

- 20 15. A method according to any preceding Claim, wherein said bodies of test fluid and reference fluid comprise flow paths and the test fluid and reference fluid are driven through said flow paths during measurement of said electrical parameter.

16. A method according to any preceding Claim wherein said measurement

cell means (1, 2, 3, 4) is composed of alumina or sapphire.

17. A method according to Claim 3 or any Claim dependent thereon, wherein said temperatures are equalised by passing said fluids through respective
5 coils of tubing (10a, 10b) in thermal contact with each other and with primary heat exchange fluid.
18. A method according to any of the preceding Claims, wherein said measurement is made on three or more bodies of fluid.
- 10 19. A method according to any of the preceding Claims, wherein two or more than two measurement cell means are provided in parallel.
20. Apparatus for determining an electrical parameter of a test fluid in relation
15 to that of a reference fluid, comprising test cell means (1, 2, 3, 4) arranged to receive a body of said test fluid and a body of said reference fluid and heat exchange means (10a, 10b, 12) for generating a flow of primary heat exchange fluid in thermal proximity to said bodies of test fluid and reference fluid.
- 20 21. Apparatus according to Claim 20 wherein said heat exchange means (10a, 10b, 12) is arranged to generate said flow of primary heat exchange fluid over the exterior of a wall (2) of said measurement cell means (1, 2, 3, 4).

22. Apparatus according to Claim 20 or Claim 21, wherein said measurement cell means (1, 2, 3, 4) is thermally symmetrical about a plane midway between said bodies of test fluid and reference fluid, said bodies being symmetrically disposed about said plane.

5

23. Apparatus according to any of Claims 20 to 22, wherein said heat exchange means comprises a metal wall (8) having one surface in contact with said measurement cell means (1, 2, 3, 4) and an opposite surface in contact with said flow of primary heat exchange fluid.

10

24. Apparatus according to any of Claims 20 to 23, wherein two or more than two measurement cell means are coupled to a common heat exchange means.

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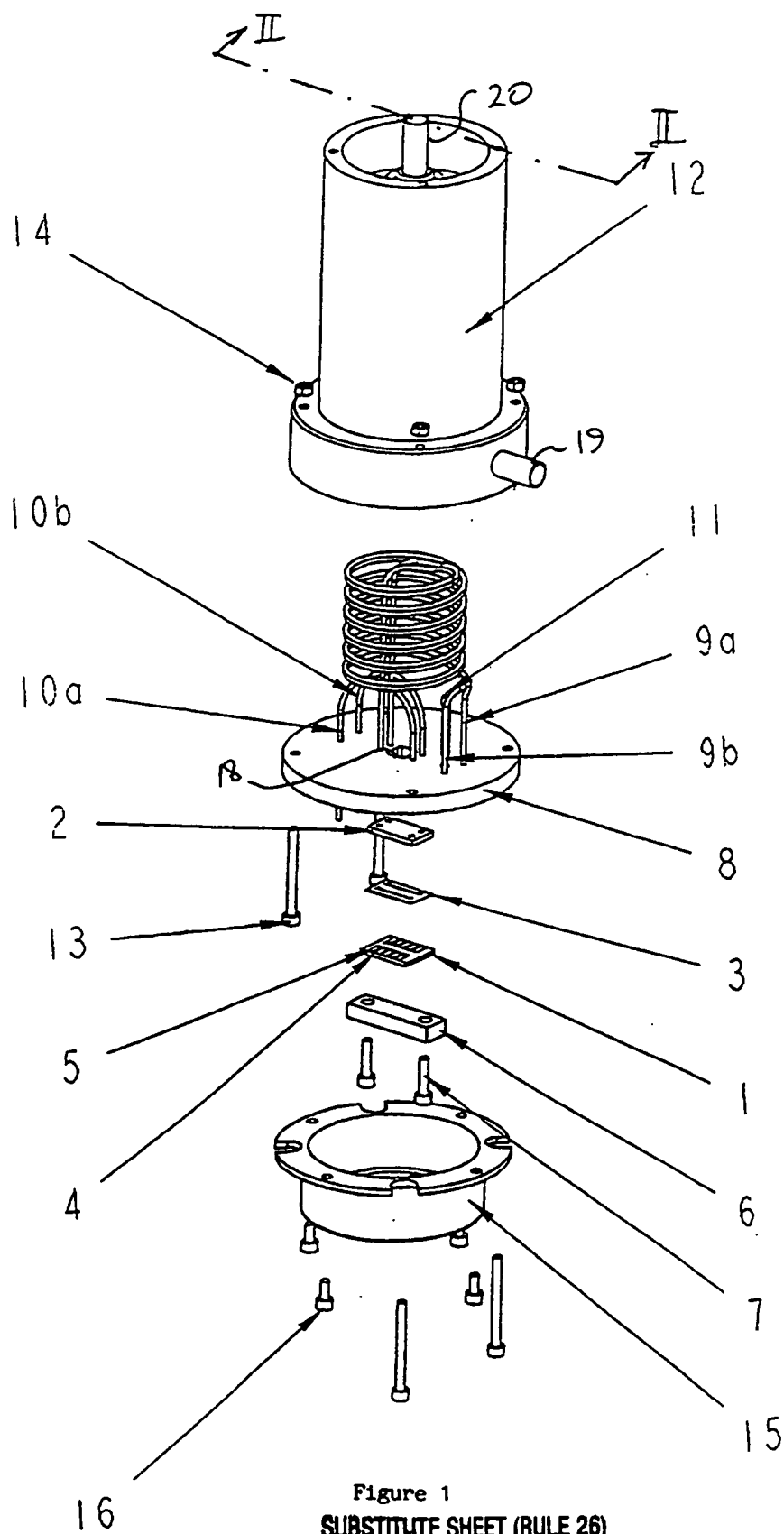


Figure 1
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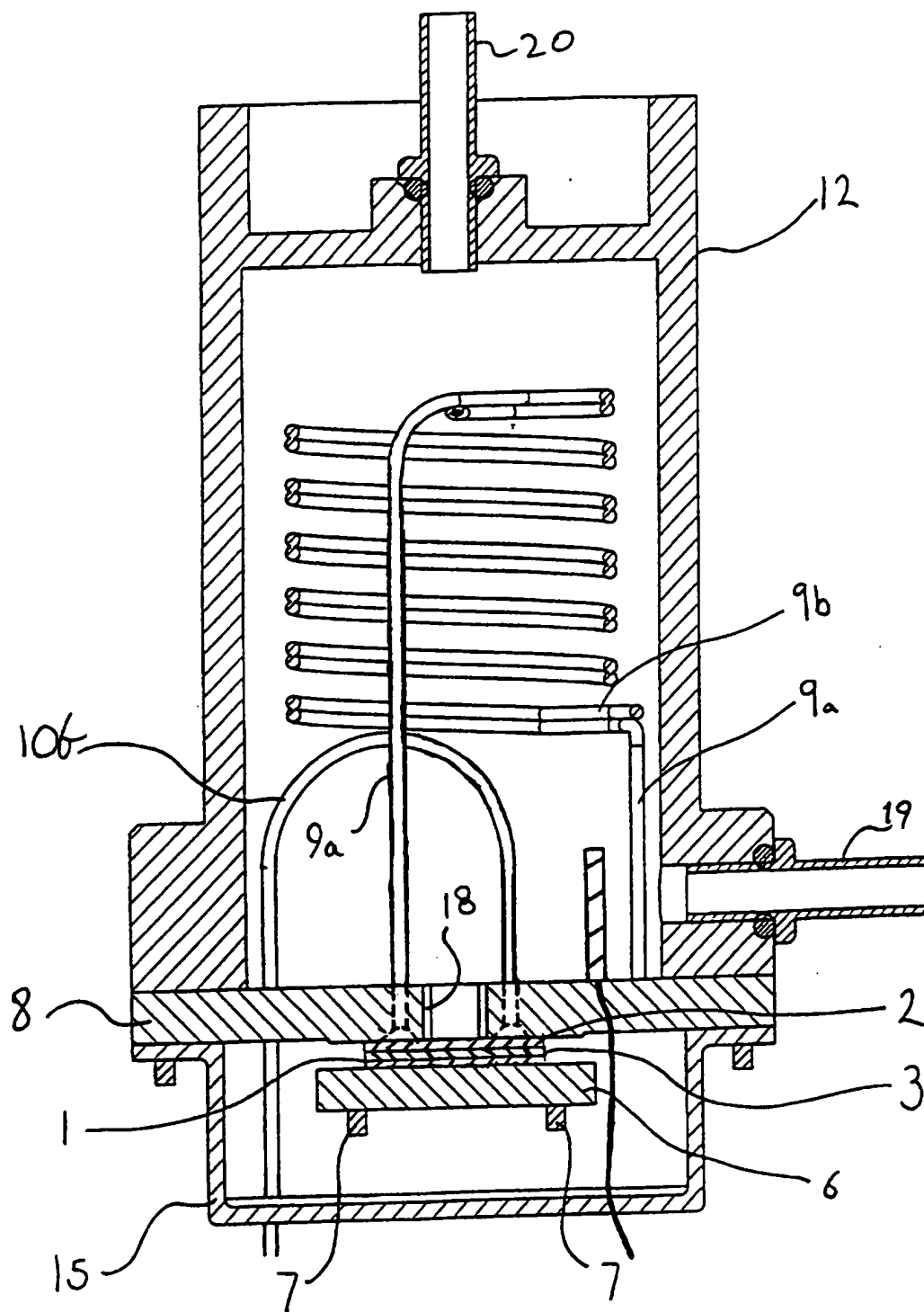


Figure 2

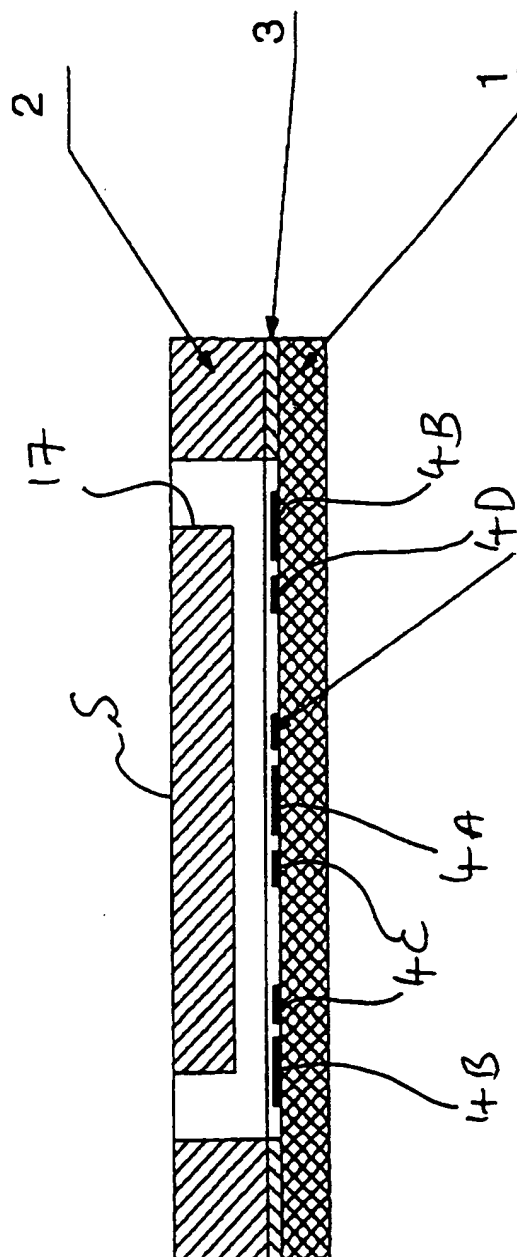


Figure 3

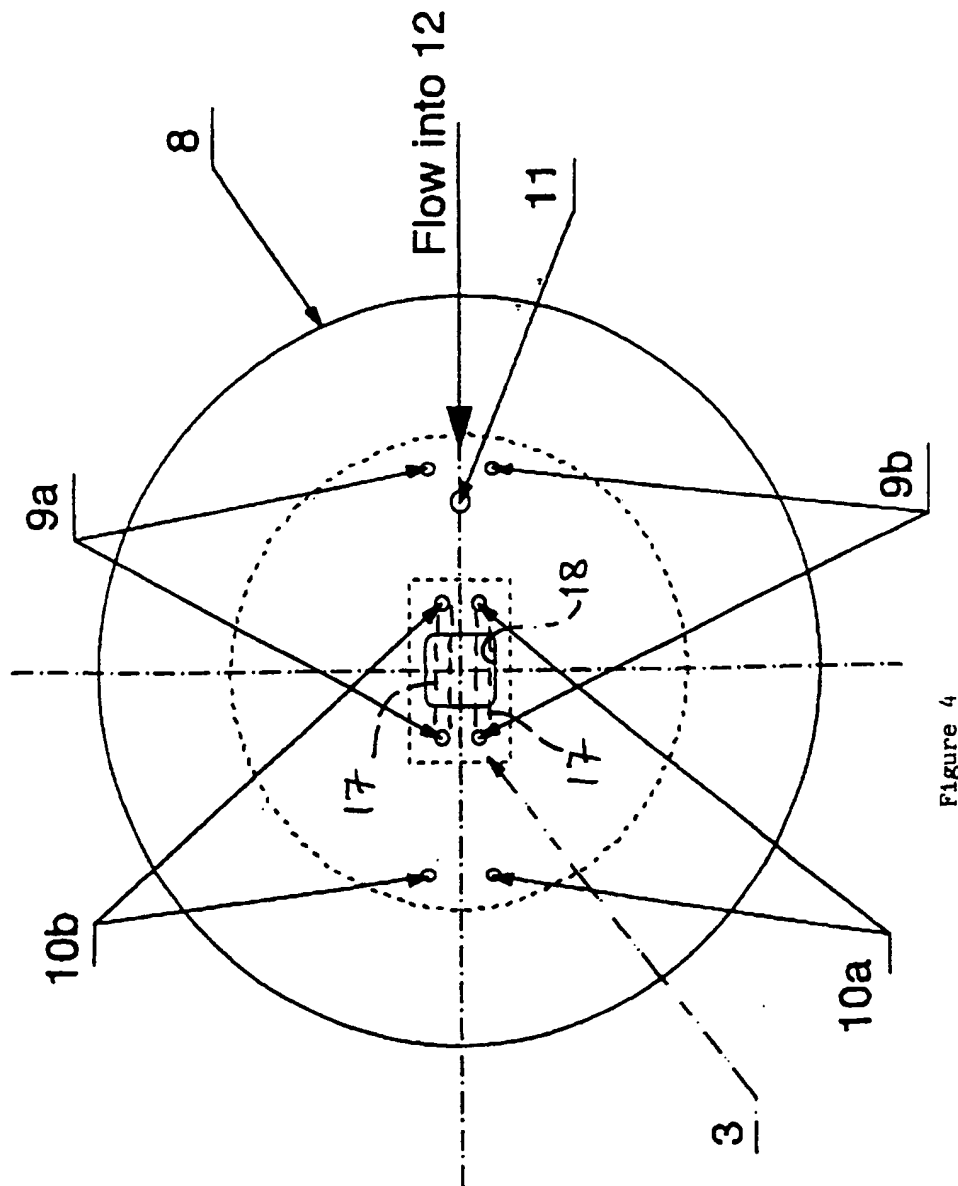


Figure 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/00098

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/06

According to International Patent Classification (IPC), or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N G01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	WO 96 04401 A (GAMBRO AB ; EDGSON RAYMOND (GB); OLDE BO (SE); OLSSON LARS FRIDE (S) 15 February 1996 cited in the application see claims 10,14,22,23,25,27; figures 9-11,8 ---	1-24
X	NL 8 300 782 A (UNIE VAN KUNSTMESTFAB BV) 1 October 1984 see page 5, line 13 - line 26; claims 1,4; figure ---	1-8,15, 17-20
X	DE 39 00 119 C (S.STILLER) 2 August 1990 see abstract; figure 1 ---	1,20
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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NL - 2280 HV Rijswijk
Tel. (- 31-70) 340-2040, Tx. 31 651 epo rd,
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 511 845 A (DAUPHINEE THOMAS M ET AL) 16 April 1985 see abstract; figures 1-3 see column 3, line 23 - line 27 ---	1-9,15, 17-24
X	US 2 422 873 A (W.F.WOLFNER II) 24 June 1947 see figures ---	1,20
X	DE 10 95 007 B (RUHRCHEMIE) 15 December 1960 see figure ---	1,20
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Information on patent family members

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